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QUARTERLY STATUS REPORT

December 15, 1953, to March 14, 1954

FABRICATION OF SYNTHETIC MICACEOUS MATERIALS

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Cleveland, Ohio

Contract NONR-483(00)
Task Order NONR-483(01)
Project NR 038-004

A. Mica Production

The problems which have been under study for the production of satisfactory electrical-grade synthetic fluor-phlogopite of the normal, boron, barium, and barium-lithium types now appear under control. The major problems appeared to be those of the need for sufficient blending to get an extremely uniform structure, and for sufficient time not only to secure complete reaction but to allow some crystal growth to occur. During this quarter the production of synthetic mica powder was carried on in a routine manner, largely to provide raw material for fabricated billets.

The production of tetrasilicic type and low temperature fabrication sodium types of mica was considered during this quarter in order to add these to the available synthetic fluor-phlogopites for test. However, experimental studies of production of these micas have not yet been completed.

B. Fabricated Synthetic Fluor-Phlogopite

A quantity of blocks 4-1/2" in diameter by 7" long were produced by hot-pressing a cold-pressed (10,000 psi) compact in a molybdenum lined CS grade graphite die at 1,000 psi and 1250°C. for normal grade fluor-phlogopite and 1,000 psi at 1050°C. for the boron type. Inasmuch as both the density and electrical properties of the normal type were superior to those of the

boron type mica and most of the demand appears to be for this grade, the stock block program for large hot-pressed billets of synthetic fluor-phlogopite will be concentrated largely on the normal type in the future. The series of billets made gave densities ranging from 2.75 to 2.77 gm/cc., showing dielectric constants averaging 6.00, with power factors between 7 and 9×10^{-4} .

Although a quantity of blocks was made, demands on the program for hot-pressed mica were such that attempts for making 9" diameter compacts, previously unsuccessful with boron type mica because of heat shock, were re-initiated to provide sufficient stock. The results of this length-to-diameter variation study can essentially be summed up as follows:

1. Although lengths up to 12" can be made with 4-1/2" diameter pressings, $\frac{L}{D}$ ratios greater than 2:1, or 9" long for this diameter, should be avoided. In general, the greater the length of column and the greater the $\frac{L}{D}$ ratio, the lower the pressure one can use with reasonable assurance that the graphite die will perform without failure.

2. Plates 2" high by 12-1/4" diameter were made of normal fluor-phlogopite without difficulty. It is believed that a number of these can be pressed at one time. As many as four 7" x 9" x 1/2" plates of both pure synthetic mica and mica with stainless steel additives have been previously made in this manner. (See third Quarterly Report, 1952.)

3. Some evidence of heat shock was obtained on pressing 9" diameter compacts of normal fluor-phlogopite 6" thick. On reducing the thickness to 4", satisfactory blocks were made.

4. With the present setup, it is believed that a ^{maximum} minimum dimension of 4-5" is necessary to prevent cracking by heat shock at the slow cooling rate used. The other dimensions are largely controlled by the amount of pressure available, the sizes of die materials available and the effect of height on die failure. Therefore, it appears that a stock block size of

9-12" diameter by 4-5" high yielding 25-55 pounds of hot-pressed product per hot-pressing may be the feasible maximum without drastically lowering the cooling rate.

In answer to a requirement from the General Electric Co., Air Turbine Division, Evandale, Ohio, for a nickel-mica compact to serve as an abradable seal in a jet engine compressor system, a series of bearing seal compositions were fabricated (See Table I). The requirement was for material soft enough so that it could be easily abraded without scoring the rotating member of the compressor system in contact with the seal at 1200°F., but of sufficient strength to resist rupturing when impacted by the rotating member. The cermet discs were made 6" in diameter by approximately 1-1/2" high from which small band segments were cut off for initial tests. Softening brought about through defluorination of the mica matrix by treating cermet compositions at 1150°C. in air appeared to increase the abradability of the seal surface at the expense of strength. The normal fluor-phlogopite-nickel powder compacts were quite machineable and no difficulty was encountered in end milling, sawing and drilling. Hot-pressed nickel-phlogopite seals were made up for testing under simulated performance conditions at the General Electric Co.

TABLE I
PHLOGOPITE-NICKEL BEARING SEAL COMPOSITIONS

<u>Identification</u>	<u>Nickel to Mica Weight Ratio</u>	<u>Compacting Pressure</u>	<u>Pressing Temperature</u>	<u>Calculated Mica Matrix Density</u>
HP-41 No. 1	2 to 1	500 psi	1200°C.	2.76 gm/cc
HP-41 No. 2	1 to 1	500 "	1200°C.	2.76 "
HP-42 No. 3	2 to 1	250 "	1200°C.	2.52 "
HP-42 No. 4	1 to 1	250 "	1200°C.	2.52 "

As the end product would involve rings up to 30" in diameter, some consideration was given to a means of pressing these more economically than by machining hot-pressed plates into circular segments. An attempt was made to produce these by cold pressing a mixture of nickel and normal phlogopite with phosphoric acid. However, on firing, sufficient attack of the nickel by the phosphoric acid occurred to destroy the bonding action. Cold-pressing and firing without bonding, although producing soft and inferior mica as compared with the hot-pressed body, appears to be preferable for this application from a technical as well as an economic standpoint, and should larger bodies be required, this process will be investigated further.

C. Examination of Product Variables in Manufacturing Synthetic Fluor-Phlogopite Billets

Now that it is possible to make reproducible lots of high grade hot-pressed mica in semi-production quantities, investigation of the effect of certain variations influencing the character and utilization of the product have been made. These are as follows:

1. Variations in Machineability

Generally, the machineability of the synthetic fluor-phlogopite is quite good, especially with the boron and normal varieties. Cutting rate equivalent to those employed with HSS tools with alloy steels are developed provided carbide tools are used with mica, the problem being that of tool wear rather than ability to cut. The barium-lithium and especially the barium micas, being much harder, are more difficult to cut. Most of the information provided on machining hot pressed fluor-phlogopite has not been very quantitative, and machineability tests were setup to give some idea of approximate optimum speeds for turning mica block and to see if variations in density could affect this variable.

For turning rounds from squares, a feed of about 8 mills per revolution, $1/8$ " depth of cut, and surface speed of 150 feet per minute was obtained, while for turning rounds from rounds, a feed from 8 to 12 mills per revolution, depth of cut from $1/8$ " to $3/16$ ", and a surface speed of 200 feet per minute was developed. In both cases, the tool was a Carboloy grade 883. No differences of machineability occurred over a range of densities from 2.5 to 2.8 gm/cc., and little differences in the boron and normal types of mica could be ascertained.

Normal mica in the same density range was evaluated for sawing, with the following results:

Sawing Conditions

Blade - 3-pitch claw buttress tooth
Blade Speed - 140 feet per minute
Blade Force - 80 pounds
Cutting Rate - 1" per minute
Stock Thickness - 2".

2. Evaluation of Cooling Under Load for Hot-Pressed Synthetic Fluor-Phlogopite

In hot-pressing synthetic fluor-phlogopite it has been determined (see fourth Quarterly Report, 1953) that if the load is not left on during the cooling cycle after hot-pressing, loss of density and visible porosity can be obtained. This is especially true of the boron variety of mica. Inasmuch as this prevents removal of the dies at high temperature to allow cooling of the material outside of the pressing equipment, considerable economic loss through tie-up of equipment is experienced. Consequently, tests were initiated to determine if the load has to be kept on during the entire cooling period or at what temperature the load can be removed without loss of density in the compact.

The tests were setup using samples of normal phlogopite with densities of 2.55 to 2.80 gm/cc. heated to various temperatures. No change

in density occurred when these samples were fired to temperatures of 600°, 800° and 900°C., but at higher temperatures the results shown in Table II were obtained. In general, the data indicated that the higher the temperature and the higher the initial density, the greater was the loss in density or gain in volume. However, this loss of density, which is attributed to the relief of trapped gases in the hot-pressed billet, only occurred when the plastic range of the synthetic fluor-phlogopite was reached. This may explain the greater difficulty experienced with boron mica in that the plastic range is not only lower but is much more widespread than for the normal variety. The data indicates that, at least with the synthetic normal fluor-phlogopite, if the hot-pressed compact is cooled to 900°C. from the pressing temperature of 1250°C., the load can then be removed without fear of loss in density. As this temperature can be reached rather rapidly, it is estimated that the total time, including heat-up, pressing and cooling time for a normal hot-pressed billet, i.e., 10 to 50 pounds, could be reduced to about four hours.

TABLE II

	Sample No.	Weight Loss %	Volume Increase %	Density gm/cc
At 1000°C.	HP-30	.015	.435	2.79
	HP-31	.026	0.0	2.759
	HP-32	.077	0.0	2.66
	HP-34	.068	0.0	2.587
	HP-33	.062	0.0	2.549
At 1100°C.	HP-30	.031	2.61	2.73
	HP-31	.107	.732	2.74
	HP-32	.132	0.0	2.66
	HP-34	.137	.296	2.58
	HP-33	.137	.477	2.54
At 1150°C.	HP-30	.062	3.7	2.70
	HP-31	.146	.915	2.73
	HP-32	.253	0.0	2.66
	HP-34	.172	.477	2.57
	HP-33	.175	.592	2.54

TABLE II

(CONTINUED)

Original Density (gm/cc)

HP-30	2.800
HP-31	2.759
HP-32	2.663
HP-34	2.587
HP-33	2.549

3. Variation in the Electrical Properties with Impurities and Density

The major impurities encountered in hot-pressed normal mica are those obtained from the die or sheath materials during the hot-pressing operation, as well as those originally in the raw materials being fabricated. The major impurities derived from the hot-pressing cans and dies are molybdenum and graphite, while the major one obtained from the raw material is magnesium fluoride.

Further work was also carried out on the variation of electrical properties with hot-pressed density for normal fluor-phlogopite, and results are shown in Table III. This indicates essentially that the dielectric constant increases with increasing density, with the power factor decreasing with increasing density. Generally, the spread shown with normal mica is much smaller and more erratic than those reported in the last quarterly report when the electrical properties of boron fluor-phlogopite were evaluated as a function of hot-pressed density.

TABLE III

ELECTRICAL PROPERTIES OF H. P. NORMAL FLUOR-PHLOGOPITE

<u>Density, gm/cc</u>	<u>Dielectric Constant</u>	<u>Power Factor</u>	<u>Loss Factor</u>
2.77	6.22	1.45×10^{-3}	9×10^{-3}
2.615	5.71	1.505×10^{-3}	8.6×10^{-3}
2.47	5.34	1.51×10^{-3}	8.22×10^{-3}

The effect of magnesium fluoride on electrical properties of hot-pressed normal fluor-phlogopite is shown in Table IV, and that of graphite and molybdenum contamination in Table V. Generally, the influence of magnesium fluoride was such that with increasing magnesium fluoride content an increase of power factor is experienced, while the same effect is true with graphite but of lesser magnitude. With molybdenum, however, little change in power factor or dielectric constant is experienced with impurities up to 1% of metal. The molybdenum in this case appears to be incorporated into the mica matrix as oxide and consequently becomes unavailable as a conducting source. This appears to be true for any metal which is introduced into the mica in fine particles.

TABLE IV
EFFECT OF MgF_2 ON THE ELECTRICAL PROPERTIES OF HOT-PRESSED
NORMAL FLUOR-PHLOGOPITE

Firing Time	5 hours	15 hours	15 hours	15 hours
Firing Temperature	1050°C.	1025°C.	1050°C.	1050°C.
Mica Content	85%	85-90%	90%	95%
MgF_2 Content	10%	5-8%	5%	3-4%
Glass Content	2%	5%	2%	1%
Density	2.77 gm/cc	2.77 gm/cc	2.79 gm/cc	2.77 gm/cc
Dielectric Constant	6.1	6.22	6.1	6.05
Power Factor	4.39×10^{-3}	1.45×10^{-3}	6.33×10^{-4}	7.15×10^{-4}
Loss Factor	2.68×10^{-2}	9×10^{-3}	3.86×10^{-3}	4.3×10^{-3}

From the contamination tests, it appears that if magnesium fluoride in the raw mica is controlled and molybdenum cans are used on the graphite dies during hot-pressing, a slight amount of contamination from the molybdenum cans, although discoloring the edges (up to 20 ppm), is not suffi-

TABLE V

EFFECTS OF GRAPHITE AND MOLYBDENUM CONTAMINATION ON THE
ELECTRICAL PROPERTIES OF HOT-PRESSED MICA

<u>Sample No.</u>	<u>Description</u>			
HP-35	100 ppm graphite contamination*			
HP-36	1,000	"	"	"
HP-37	10,000	"	"	"
HP-38	100	"	molybdenum contamination**	
HP-40	1,000	"	"	"
HP-39	10,000	"	"	"

<u>Sample No.</u>	<u>Density gm/cc</u>	<u>Dielectric Constant</u>	<u>Power Factor</u>	<u>Loss Factor</u>
HP-35	2.762	6.16	1.47×10^{-3}	9.05×10^{-3}
HP-36	2.757	6.05	1.60×10^{-3}	9.60×10^{-3}
HP-37	2.773	6.53	3.33×10^{-3}	21.80×10^{-3}
HP-38	2.793	6.24	2.73×10^{-3}	17.05×10^{-3}
HP-40	2.80	6.20	2.43×10^{-3}	15.10×10^{-3}
HP-39	2.844	6.43	2.08×10^{-3}	13.40×10^{-3}
Control	2.75	6.16	1.20×10^{-3}	6.79×10^{-3}

*

-325 Mesh Acheson Ink Graphite Powder

**

-200 Mesh Molybdenum Powder

cient to harm or severely modify the properties of the hot-pressed mica. The graphite contamination which is extremely unsightly is also not particularly harmful to the electrical properties, but in the interest of uniformity and preserving the die materials, should be avoided. It must be emphasized that the contamination studies were carried out on one particle size of contaminant, and that larger particles of graphite, for instance, would presumably have greater effect than large amounts of small particles. However, the actual contamination is in the form of the fine particles indicated and appears to be more unsightly than harmful.

However, since the coarser crystal 15-hour mica have been used, little contamination from diffusion of the molybdenum into the phlogopite has been noticed. Apparently, with less surface area of mica, the rate of reactivity or diffusion of can into compact has been severely curtailed.

D. Special Fabrication Studies

Although all of the pieces which have been required for distribution to date can be made by machining from hot-pressed blocks, this method is not suitable for competition with a great many parts (indeed, this may eventually prove to be the majority) which are now being made from ceramic insulators such as steatite, forsterite, etc. Most of these are made to small regular shapes, usually as tubing or tubular configurations, by the extrusion process. Although it is possible to make these by machining hot-pressed mica, for many shapes it is prohibitively expensive, and as a consequence, because of cost factor, hot-pressed synthetic fluor-phlogopite appears to be priced out of many applications wherein electrically it is very satisfactory.

Although synthetic fluor-phlogopite can be fabricated by cold-pressing a mixture of phosphoric acid and phlogopite followed by firing and sintering (developed by the Electrotechnical Laboratory, U. S. Bureau of Mines),

and the material can be slip cast into electrical shapes (developed and reported by the Brush Beryllium Company, first Quarterly Report, 1953), the resulting densities from these operations are usually lower than those from hot-pressing. However, for many applications where electrical parts are used, this may be permissible if there is a substantial economic gain. With this in mind, preliminary investigational experiments were undertaken on the extrusion of synthetic fluor-phlogopite in order to make small rods and irregular shapes. Two approaches were used, one with -35 mesh phlogopite plasticized with starch and water, and the other using phosphoric acid mixed with the powdered raw material. The batches were thoroughly blended by mulling prior to extruding. The following extruded densities were obtained with 3/4" diameter rods 12" long.

TABLE VI
EXTRUDED FLUOR-PHLOGOPITE ROD DENSITIES

<u>Phlogopite Type</u>	<u>Plasticizer</u>	<u>Density, gm/cc</u>
Normal	Starch & Water	1.85
Boron	Starch & Water	1.68
Normal	Phosphoric Acid	2.17
Boron	Phosphoric Acid	2.33

The phosphate bonded boron mica and the starch bonded normal variety appeared to produce the most favorable extruded material. However, the final evaluation will rest with the determination of such properties as strength, dielectric constant, power factor, etc. All of the densities obtained are considerably lower than those derived from hot-pressed material.

Another experimental fabrication technique investigated was the direct hot-pressing of reacted briquettes in order to eliminate the grinding,

screening and cold-pressing now used. A block 9" in diameter by 6" high was pressed from a normal reacted sinter mass to 2.73 gm/cc. under normal conditions. However, upon examination of the compact, cracking was found to be present in the interior. This apparently had originally occurred during reaction and the hot-pressing step was insufficient to weld up all the initial cracks. The method, however, seems to be perfectly satisfactory to use with sound reaction cakes, and appear capable of producing a good body to density with considerably less surface contamination than normally occurred when hot-pressing ground powder. However, the inability to determine effectively the extent of cracking after the reaction step could modify considerably the use of this process in production.

E. Evaluation

During the first quarter of 1954, approximately twenty shipments with three-fourths consisting of fabricated articles and one-fourth powder, were sent to interested companies for test purposes. This is about normal for the period covered, although one change which appears quite favorable is now appearing in the distribution picture. During the indicated quarter, unlike the subsequent periods, about one-third of the pieces were direct sales rather than samples. These were the results of re-orders, essentially indicating the sample program has developed sufficient interest in large-scale testing and/or some small-scale utilization.

Hot-pressed normal fluor-phlogopite can now be successfully machined by surface grinding or cut-off tools into sections of 20 mill thickness and a number of samples are under test. The imperviousness to vacuum of these samples appears erratic and it is indicated that samples of this type need densities higher than normally achieved when pressing large blocks (2.73-2.78 gm/cc.). Samples of higher density mica are now under test for potential use under high vacuum.

F. Plans for Future Work

1. An integrated report on the fabrication of mica carried on under this contract is being assembled for submission as a paper to the American Ceramic Society. This will be a revision (to include the latest information) of a paper presented at the Pacific Coast meeting in San Francisco last October of the A.C.S. and will be presented at the American Ceramic Society meeting in Chicago (Materials and Equipment Division) on April 22, 1954, under the title "Fabrication of Synthetic Fluor-Phlogopite Mica Ceramics".

2. As about 85 recipients of samples for special tests under this contract have not reported their results, a canvass of all companies receiving such samples will be undertaken during the next quarter in order to complete the utilization potential developed from this work.

3. More information will be developed on variables affecting the fabrication and use of synthetic phlogopite. These include particle size, bonding strength and isotropy of properties as a function of fabrication variables, as well as further studies on the thermal shock problem which now appears to be the most limiting factor in the fabrication of synthetic mica.

4. Further studies on extrusion and the properties resulting therefrom, as well as some work in the cold-pressing and firing of phosphate bonded barium and barium-lithium mica will be made. It is hoped that products of interest can be developed from these types of mica by the cold-pressing and sintering of the phosphate bonded particles, as the products resulting from hot-pressing are far too strong and tough to be machined, although they have excellent electrical properties.

5. Production of sodium and tetrasilicic types of synthetic fluor-phlogopite will be investigated to add these two potentially useful micas to the products under distribution.